Accumulation of nitrogen in the snowpack of urban parks and its connection to dog activities.

University of Helsinki
Master’s programme in
Environmental Change and
Global Sustainability
Master’s thesis
28 July,2020
Name : Gausul Azam
(Supervisors: Johan Kotze & John Allen)

Tiedekunta – Fakultet – Faculty Faculty of Biological and Environmental Sciences	Koulutusohjelma – Utbildingsprogram – Degree Programme : Environmental Change and Global Sustainability	
Tekijä – Författare – Author Gausul Azam		
Työn nimi – Arbetets titel – Title Accumulation of nitrogen in the snowpack of urban parks and its connection to dog activities.		
Oppiaine/Opintosuunta – Läroämne/Studieinriktning – Subject/Study track Environmental Change and Global Sustainability (Study track: Environmental Change)		
Työn laji – Arbetets art – Level Master's Thesis	Aika – Datum – Month and year 28 July,2020	Sivumäärä – Sidoantal – Number of pages 29+(appendices 2)

Tiivistelmä – Referat – Abstract

Dog activities (urination and defecation) can be a source of nitrogen accumulation in the snowpack of urban parks. Urban parks are commonly visited by urban residents and excessive buildup of nitrogen in snowpack can be a health concern. This accumulation of nitrogen in snowpack may wash away during spring with the runoff of melting snow, which can cause the eutrophication and deterioration of lake ecosystems. In this study, I investigated the concentration of some nitrogen-related compounds along with a few physical parameters in the snowpack of urban parks and compared these between areas with high dog activities and areas with no dog activities. I hypothesized that, nitrogen concentrations will be higher in areas with high dog activities, like snowpack beside paths than in areas with no dog activities. The study was performed in 10 parks of two cities in Finland; Helsinki and Lahti. In these parks, samples were collected from snowpack immediately next to walking paths (path edge), and in control areas 8 m away from these paths, where dogs were unlikely to visit. Samples were collected from February to April of 2019. The concentration nitrogen from snow samples of both parts of parks were compared.

The study showed that, the concentration of most nitrogen species, e.g. Total Nitrogen (TN), ammonium (NH_4^+), Total Organic Nitrogen (TON), and electrical conductivity followed a similar pattern of having higher values in snow from path edges where dog activities were the highest. However, the concentration of NO_3^- and pH values were both slightly lower in the path edge samples compared to control areas undisturbed by dogs, but differences were not statistically significant. Information from this study can be useful for understanding the connection between dog activities and nitrogen build up in snowpack of urban parks, and can also be helpful for designing urban parks by considering environmental and health effects of nitrogen accumulation in the snow from dog activities. My findings can also be useful to urban waterbody related studies, e.g. eutrophication, and the accumulation of nutrients in lakes.

Avainsanat – Nyckelord – Keywords
Nitrogen, Urban Park, snowpack, dogs

Ohjaaja tai ohjaajat – Handledare – Supervisor or supervisors
Johan Kotze & John Allen

Säilytyspaikka – Förvaringställe – Where deposited

Helsingin yliopiston kirjasto, Helsingfors universitets bibliotek, Helsinki University Library

Muita tietoja – Övriga uppgifter – Additional information

Abbreviations

GLMM	General Linear mixed models
N	Nitrogen
NH_4^+	Ammonium
NO_3^-	Nitrate
TN	Total Nitrogen
TON	Total Organic Nitrogen

Table of content

ABBREVIATIONS i

1 INTRODUCTION.. 1

2 MATERIALS AND METHODS 6

2.1 Study area 6

2.2 Study design.. 9

2.3 Field sampling 10

2.4 Laboratory analysis 12

2.4.1 Physical parameter analysis.. 12

2.4.2 Chemical parameter analysis 13

2.5 Statistical analysis 15

3 RESULTS 16

3.1 Helsinki and Lahti 16

3.2 Two sampling visits in Lahti 18

4 DISCUSSION.. 21

4.1 Concentration of nitrogen-related compounds in urban parks 21

4.2 Intra-seasonal variation of nitrogen concentrations in urban snowpack 22

4.3 pH and conductivity in the snowpack of urban park 23

8 ACKNOWLEDGEMENTS 25

REFERENCES.. 26

APPENDIX.. 30

1 Introduction

Urban parks are an essential part of modern cities around the globe. They play important roles not only from social (e.g. decreased criminal and anti-social behaviour), health (e.g. increased physical activities and fitness, decreased mental distress and mental disorder) and recreational perspectives, but also from an environmental perspective (e.g. noise filtering, air purification, microclimate stabilization, and controlling stormwater runoff) (Coombes et al., 2010; del Saz Salazar and Menendez, 2007; Hartig et al., 1991; Nowak et al., 1998; Tzoulas et al., 2007). Urban parks provide a multitude of functions and having parks and green spaces in urban areas is a common goal for policy makers in both developed and developing countries (Nowak et al., 1998). Cost-benefit analyses have shown that parks have many benefits that cannot always be converted into monetary values (Wolfe and Patz, 2002). Recognizing these benefits, the World Health Organization encourages local administrators and policymakers to increase urban green spaces and to maintain a minimum of 9 m^2 per capita (Edwards and Tsouros, 2006). As a result, ecosystem services that urban parks are providing can be vital as it relates to human health and health of the environment. However, the ecosystem services that parks provide can be deteriorated by some human activities, one of which is pet ownership.

Snowfall at higher latitudes is a common natural phenomenon in winter, resulting in the formation of snowpack where a large part of the soil is covered with snow. Urban areas at higher latitudes also face the same scenario. In 2012, the Helsinki municipal authority removed approximately 3.2 to 4.5 million m^3 of snow (Keskinen, 2012). Similarly, 21-22 million € had been allotted in 2016 only for the removal of snows from the municipality of Helsinki (Särkkä, 2016). The same situation is common for urban parks, where a seasonally persistent snowpack may form during winter months. Hazardous compounds present in the atmosphere can be deposited with snowfall, and may remain in the environment for long periods of time (Abdel-Shafy and Mansour, 2016). Snow may play a role as a transport tool for various contaminates (Reinosdotter and Viklander, 2005) such as, e.g. chlorides, sulphates, suspended solids, and metals (Viklander, 1999). Snow can trap air pollutants

(Nazarenko et al., 2016) regardless of its distance from urban areas (Na et al., 2011). Excessive nitrogen accumulation may have potential negative effects on human health and the environment (Wolfe and Patz, 2002). High levels of air- and water-borne nitrogen are linked to respiratory ailments, cardiac disease, and several types of cancer (Pope Iii et al., 2002).

Two studies exist on the presence of contaminants in snow in the city of Lahti, Finland. Pollution in roadside snow due to traffic intensity showed that pollutant concentrations are higher near traffic roads and decreased gradually with distance from the roads (Kuoppamäki et al., 2014). The second study investigated the deposition of polycyclic aromatic hydrocarbon contamination in the soils of snow disposal sites, and found the higher level of polycyclic aromatic hydrocarbon in disposal site than control (Allen, 2016).

Apart from these pollutants in urban snow, there is another interesting aspect in urban parks that is not well studied. Having pets is a common practice in many parts of the world, especially in developed countries (Reese, 2005). Dogs are common pets and urban parks are common places for the recreational activities of citizens and their pets. Dog urination and defecation are common issues in parks. During summer, dog urine enters the soil immediately, but in winter, much of the urine is trapped (suspended) in the snow (Fig. 1), only to be released at the end of winter and/or during snowmelt. As such, there can be a gradual build-up of nitrogen in the snowpack of urban parks during winter.

Figure 1. Evidence of dog urination in snowpack in Kurkipuisto Park, Helsinki, Finland (Photo: Gausul Azam, 25 January, 2019).

The most abundant element in the atmosphere is nitrogen (around 80%) and one of the vital parts for life as it forms many important biomolecules such as amino acids and nucleotides (Camargo and Alonso, 2006). It is a colourless, odourless and tasteless gas, and is ranked as the 4th most common chemical element in living tissues after carbon, oxygen and hydrogen (Campbell, 1990). The nitrogen cycle is an important biogeochemical cycle on the world. Nitrogen flows among the atmosphere, terrestrial, aquatic and marine ecosystems by forming different chemical formations. These transformations of N happen through several biological and physical processes for example, fixation, ammonification, nitrification, and denitrification. Atmospheric nitrogen is the biggest source of natural nitrogen. Human activities (e.g. agriculture, industrialization, transportation and urbanization) have increased the input of nitrogen in terrestrial ecosystems (Galloway et al., 2008). However, very high levels of nitrogen, or an excess of nitrogen, can deteriorate the functioning of ecological systems (Camargo and Alonso, 2006).

Broadly speaking, the nitrogen cycle has five steps in which nitrogen turns into different chemical formations:

- Nitrogen Fixation (N_2 to NO_3^- or NH_4^+)
- Nitrification (NH_3 to NO_3^-)
- Assimilation (here NH_3 and NO_3^- are incorporated into biological tissues)
- Ammonification (organic nitrogen compounds to NH_3)
- Denitrification (NO_3^- to N_2)

Atmospheric nitrogen (N) deposition deriving from anthropogenic sources represents a significant N input to most regions on Earth (Galloway et al., 2004). Atmospheric nitrogen can be deposited with precipitation. Precipitation usually contains atmospheric N in the form of NH_2. Total N deposition is typically higher in urban areas compare to rural areas as a result of higher human inputs (Bettez and Groffman, 2013; Fang et al., 2011). Atmospheric deposition of N does not vary greatly spatially (Liu et al., 2011). Therefore, the background levels of N in the snows of parks are considered to be the same across my study design, while nitrogen deposition from dog activities was the focal point.

Dog urine consists of 95% water and 5% organic materials and ions that are water soluble (Kara Rae, 2017). Urea, $CO(NH_2)_2$ is the main organic compound of urine (Fig. 2). Urine deposited in snow can increase the levels of NH_4^+ and NO_3^- in addition to background nitrogen levels derived from atmospheric deposition (Davies et al., 2013).

Figure 2. The structure of urea.

In spring, snowmelt causes runoff that transports pollutants and nutrients from the land surface to nearby water bodies such as lakes and streams (Halstead et al., 2014). This phenomenon may lead to the eutrophication and deterioration of water quality (Conley et al., 2009), and can destroy aquatic ecosystems and may indirectly affect human health (Anderson et al., 2002). As a result, studies investigating the accumulation of nitrogen due to dog urination and defecation in urban parks can be important to understand the role of dog activities on nitrogen dynamics in parks, and subsequently on park management by considering these health and environmental concerns.

This study investigates the accumulation of nitrogen due to the activities of dogs, in the snowpack of urban parks during winter. A review of the literature shows that atmospheric deposition remains the same over a certain area (Liu et al., 2011), and as such, the activities of dogs in terms of their urination behaviour during winter is expected to be an extra source of N in the snowpack. A comparison of nitrogen levels between areas with high dog activities and areas with no dog activities was done in this study. My primary research question is the following:

- Does nitrogen accumulate in snow banks next to paths compared to areas further away from these paths and other infrastructures?

I hypothesise that,

- Nitrogen concentrations will be higher in areas with high dog activities, like snowpack beside paths than in areas with no dog activities.

To my knowledge, this is one of the first studies to investigate the activities of dogs, mainly urination, in the snowpack of urban parks.

2 Materials and methods

2.1 Study area

The study was performed in two cities in Finland, Helsinki (60°10′15″N 24°56′15″E) and Lahti (60°59′N 025°39′E). Finland is located in northern Europe, and has a cold continental type climate (Finnish Meteorological Institute, 2020). The population of Finland is about 5.5 million people in 2020 according to the last determination of Worldometer elaboration of the United Nations (Finland Population-Worldometer, 2020). 86.1% of this population lives in urban areas (Finland Population - Worldometer, 2020). Population density in Finland in 2020 is 18 people per km^2 (Finland Population - Worldometer, 2020). Winter in Finland is longer compare to most countries, specifically in Lapland which has the greatest amount of snow (Snow statistics - Finnish Meteorological Institute, 2020). Annual snowfall in different locations in Finland may vary significantly from year to year (Finnish Meteorological Institute, 2020).

This study focused on 10 parks in two cities of Finland, Helsinki and Lahti (Fig. 3). Helsinki is the capital of Finland, with the capital region having a population of 558 457, with a population density of 3 041 per km^2 (Finland Population - Worldometer, 2020). Lahti is the 7th most populated city and 8th largest city of Finland with a population of about 119 823 and a population density of 261 per km^2 (Tilastokeskus, 2020).

Temperature of Finland fluctuates between -35° C and 35 °C within a year, and winter lasts for 135 to 145 days with snow cover from the end of November until mid-April. The average depth of snow at the end of March is 10 to 20 cm (Snow statistics - Finnish Meteorological Institute, 2020).

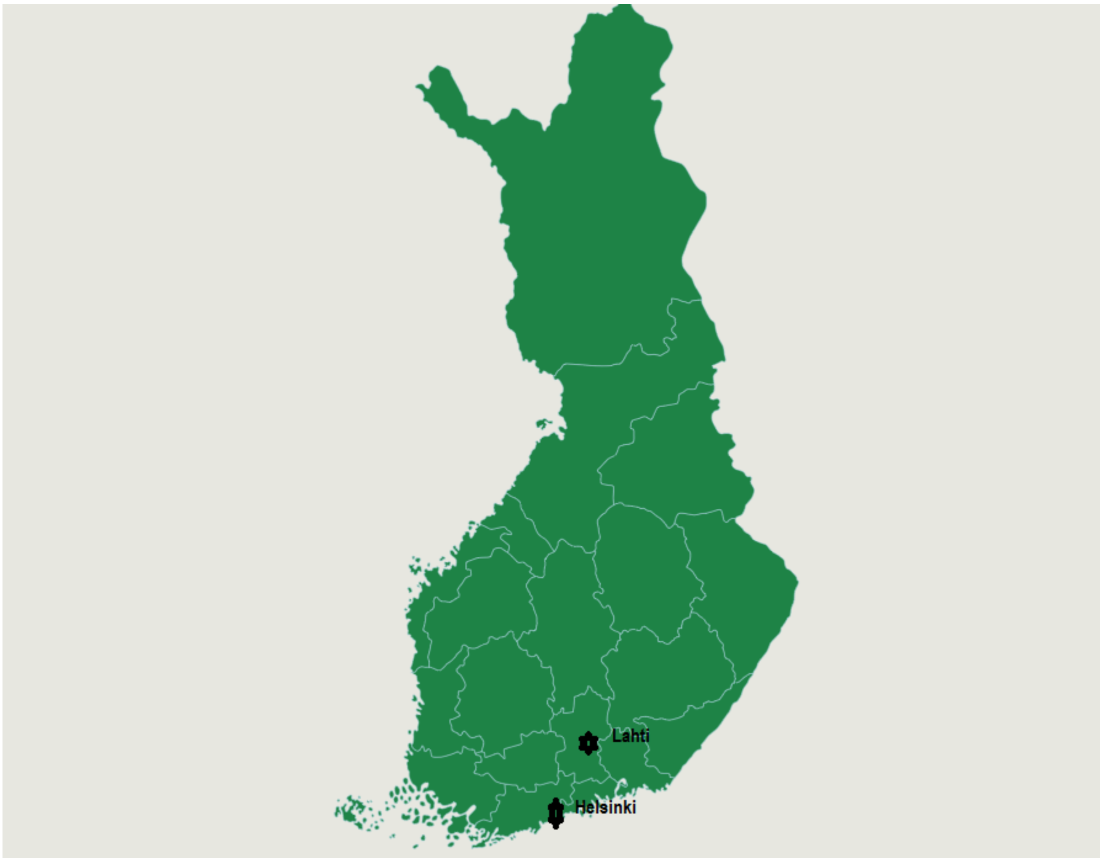

Figure 3: Map of Finland (with the location of Helsinki and Lahti).

Ten parks were selected for this study, five in Helsinki and five in Lahti. During winter time, parks are usually covered by snow.

The parks selected in Helsinki (Fig. 4), included:

- Vanha kirkkopuisto
- Hesperian puisto
- Munkkiniemen kartanon puisto
- Kurkipuisto
- Vallilanlaaksonpuisto

Figure 4: Parks in Helsinki selected for the study (Google Earth, 2020).
(1= Munkkiniemen kartanon puisto, 2= Kurkipuisto, 3=Vallilanlaaksonpuisto,4= Hesperian puisto,5= Vanha kirkkopuisto)

The parks selected of Lahti (Fig. 5) are:

- Kevätkadun puisto
- Piippupolkupuisto
- Kirkkopuisto
- Erkonpuisto
- Anttilanmäenpuisto

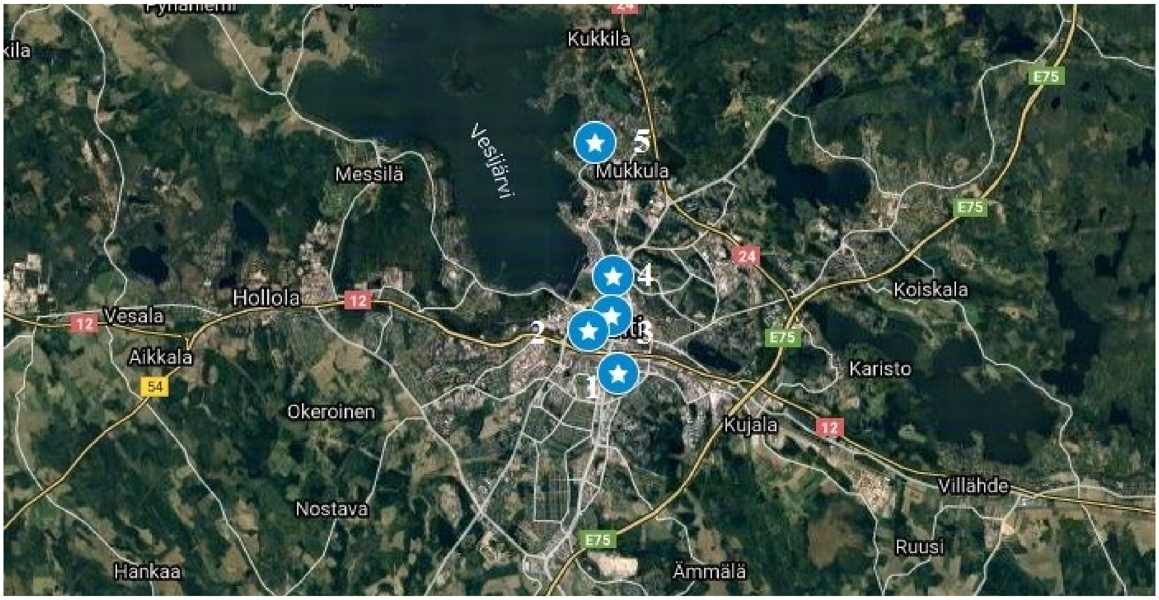

Figure 5: Parks in Lahti selected for the study (Google Earth, 2020).
(1= Anttilanmäenpuisto , 2= Erkonpuisto, 3= Kirkkopuisto, 4= Piippupolkupuisto,5= Kevätkadun puisto)

2.2 Study design

Initial study plan

My initial plan was to calculate differences in N concentrations between control snow samples (more than 8 m from any infrastructures and trees in urban parks) and urban park infrastructure (paths, trees and poles). The hypothesis was that N concentrations would be higher in snow samples close to infrastructure rather than controls. However, during the first field excursion on 25-26 January, 2019 it became clear that this design was flawed because, unlike during summer months, dogs do not seem to have access to trees or poles (which were surrounded by deep snow), but rather urinate on the snowpack next to paths. Based on this observation, I changed the research plan and design and focused on differences in nitrogen between the edges of paths in parks compared to control plots more than 8 m from these paths.

Final study plan

The final plan was then to investigate differences in nitrogen concentrations and other parameters between areas with high dog activity, such as the path edge in urban parks (see Fig. 1) and areas with no dog activities. A +8 m distance from any infrastructure such as pathways, poles and trees were selected as controls, which assumed to have no input from dog urination as dogs usually do not have excess there due to heavy snow deposition.

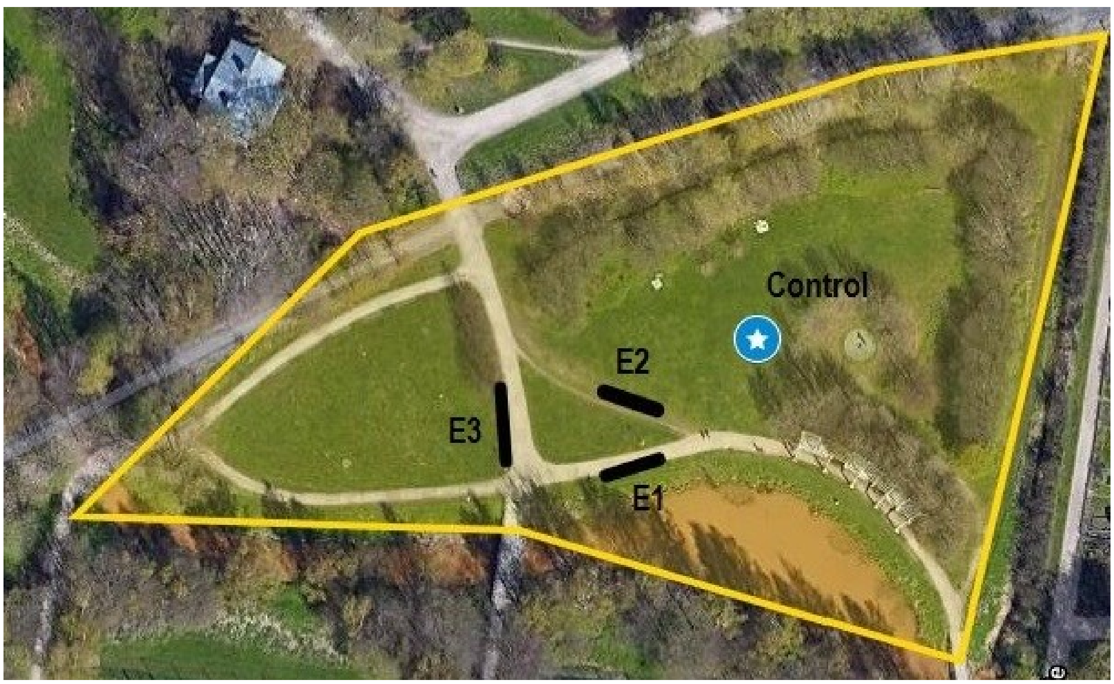

Figure 6: Schematic feature of a park according to the study design. E1, E2 and E3 represent three path edge lines (10 m) and the star represents the control point.
(Park Name -Vallilanlaaksonpuisto)

2.3 Field sampling

The first sampling event took place during 25-28 February 2019 in 10 parks of both cities (Helsinki and Lahti). The second sampling event took place during 1-2 April 2019 in the five parks in Lahti only. The original plan for the second sampling event was to sample all 10 parks in both cities, but snow in the parks in Helsinki had already melted in April.

For each park, three path segments were established and samples were taken from the edges of these paths (Fig. 6). The path length for taking samples was always 10 m and the starting point was selected randomly by tossing a coin. Along this 10 m line, samples were taken at 2 m intervals (five in total). At each of the 2 m sampling points, a 1 m^2 quadrat (Fig. 7) was placed at the path edge and five subsamples taken within the quadrat. One 1 m^2 quadrat was used to take samples from the control point.

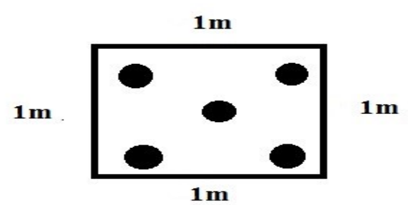

Figure 7: 1 m^2 sampling square (the five black dots represent five sampling points inside every square). The quatrat was actally 1 m2, so each side is 1m long.

I used an iron cylinder pipe to take the samples, and I tried to get the maximum depth of ice as a sample (see Fig. 8). For this reason, I used a hammer as the bottom of snow was usually hard. The depth of snow was recorded and an average value for snow depth was calculated after sampling of each path edge length of 10 m. Snow samples were kept in 5 or 10 L buckets and separate buckets were used for each path edge line and control with their respective sampling code.

Figure 8: Image of sampling in a park with all the equipment used. (Park name: Kevätkadun puisto)

2.4 Laboratory analysis

For this study, two types of parameters were measured, physical and chemical parameters. I chose to measure four chemical components; Total Nitrogen (TN), Ammonium (NH_4^+), Nitrate (NO_3^-) and Total Organic Nitrogen (TON) to evaluate the concentration of Nitrogen in snow samples. Two physical parameters, pH and conductivity were also measured.

2.4.1 Physical parameter analysis

All samples in their buckets were transferred to the University of Helsinki's Alma Laboratories in Lahti and were kept for 48 hours in cold storage at 4 °C. Later the samples were kept at room temperature for a short period of time so that the ice completely melted. Then, samples were filtered with coffee filter paper and total volume of samples per pathway segment were measured. From the total sample, a volume of approximately 200 ml was taken and these water samples were kept in 2 bottles of 100 ml each, where one bottle was kept in a freezer at -20 °C for further chemical analysis while the other sample bottle was used to measure conductivity and pH immediately.

A Mettler Delta 340 pH meter was used to measure pH. A WTW Cond 330i meter was used to measure electric conductivity.

2.4.2 Chemical parameter analysis

The 100 ml sample bottles that were kept in the freezer at -20 °C were put at room temperature for one day prior to analysis. The thawed samples were placed in 10 ml capsules for analysing Total Nitrogen (TN), NH_4^+ and NO_3^-. Six 10 ml capsules were used in the analyses, two for analysing each of the three nitrogen components; Total Nitrogen (TN), NH_4^+ and NO_3^-. The procedures of measured chemical parameters are discussed in the following part:

Ammonium (NH_4^+) and nitrate (NO_3^-)

The samples that were kept in a freezer at -20 °C were placed at room temperature for one day prior to analysis. NH_4^+ and NO_3^- concentration was measured via the colorimetric microplate method (Sims et al., 1995).

Samples were pipetted into 96-well microplates (> 300 µl/well) with two standard curve (one in the start and one in the end) and also with an external quality control solution (NH_4^+ ion ERA #985; NO_3^- ion ERA #991) for every curve and a quality control and standard check solution in the middle (after every nine samples) . The Processes used for preparing and the addition of reagents to microplates, as well as the analysis of microplates on microplate reader (Victor 3 microplate reader, Fig. 9) were done by following Sims et al. (1995) and Doane and Horwáth, (2003). Concentrations of samples were measured by using standard curves and they were interpolated between the two standard curves depending on the position of the sample pipetted. The measured absorbance values were calibrated with standards and controls and finally the NH_4^+ and NO_3^- concentration was transformed to μgL^{-1}.

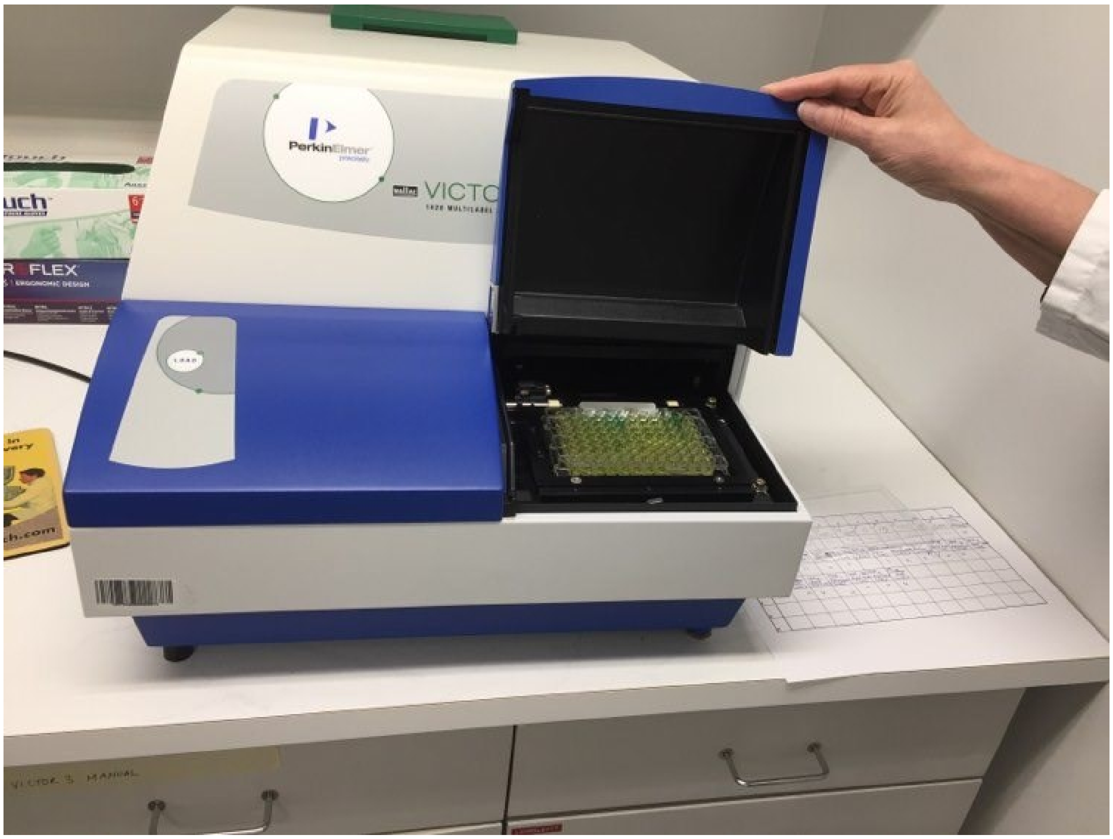

Figure 9: Microplate reader (Victor 3) in Alma lab, Lahti.

Total Nitrogen (TN)

TN concentration was also measured via colorimetric microplate technique (Sims et al., 1995). As previously discussed for the measurement of NH_4^+ and NO_3^- , for TN also samples were pipetted into 96-well (> 300 µl/well) and two standard curves and one external control solution had been used. The processes of making reagents and adding procedures as well as reading of microplates in microplate reader (Victor 3 microplate reader, fig. 9) was done by following the techniques of Miranda et al, 2001. Concentrations of samples were measured by using standard curves. The measured absorbance values were calibrated with standards and controls and finally the concentration was transformed to μgL^{-1}

Total Organic Nitrogen (TON)

TON concentration was calculated from the measured concentration values of NH_4^+, NO_3^- TN.

I considered, Total Nitrogen (TN) = Ammonium ($NH4^+$) + Total Organic Nitrogen (TON) + Nitrate (NO_3^-)

So, TON = TN – ($NH4^+$ + NO^{3-})

2.5 Statistical analysis

General Linear mixed models (GLMM) using the *lme* function in the nlme package in R (R Core Team, 2019) were used to test my hypotheses. Two types of analyses were performed. First, I used data from all 10 parks in both cities to test for differences in physical and chemical parameters (response variables) between path edge and control plots (treatment factor with two levels). Since each park had multiple sampling points, I added park identity, nested in city as random terms to the models. Secondly, I analyzed Lahti data only, adding visit to the models (two visits to parks in Lahti). The random term for this model was park identity Histograms and the Shapiro-Wilk Test was used to determine normality in the response variables, and if not, transformations were used to normalize the data. P value which was less than 0.05 is considered as significant.

3 Results

Concentrations of four chemical parameters, total nitrogen (TN), ammonium (NH_4^+), nitrate (NO_3^-) and total organic nitrogen (TON), and two additional variables; pH and electrical conductivity, were analyzed in this study. Results are presented in Tables 1 and 2, and Figures 10 and 11, and are discussed below.

3.1 Helsinki and Lahti

GLMM results of the six parameters between the control and path edge treatment from the first sampling event in both cities, Helsinki and Lahti are presented in Table 1 and Fig. 10. Among the four chemical parameters, Total Nitrogen (TN), Ammonium (NH_4^+) and Total Organic Nitrogen (TON) had higher concentrations in path edge samples than the control samples. For Nitrite (NO_3^-) however, path edge samples had a lower concentration than control samples. In the case of pH, control samples had higher pH values than path edge samples, but the difference was not statistically significant. Conductivity was higher in the path edge treatment than the control treatment and the difference is significant. Raw parameter values are presented in Appendix 1.

Table 1. GLMM results. Coefficient (± standard error, SE) values of each of the variables measured from snow collected in the parks of Helsinki and Lahti during 25-28 February 2019. Control sites are in the intercept. Treat (Edge) represents the difference between path edge and the control. Some parameters were log transformed to normality to satisfy test assumptions.

Parameter		Intercept	Treatment (Edge)
TN (log)	Value (±SE)	5.525 (0.478)	1.353 (0.339)
	P	< 0.001	< 0.001
NH4+ (log)	Value (±SE)	4.357 (0.353)	1.286 (0.289)
	P	< 0.001	< 0.001
NO_3^-	Value (±SE)	135.603 (24.208)	-34.511 (16.230)
	P	< 0.001	0.0522
TON (log)	Value (±SE)	4.324 (0.441)	2.287 (0.445)
	P	< 0.001	< 0.001
pH (log)	Value (±SE)	1.920 (0.023)	-0.019 (0.011)
	P	< 0.001	0.103
Conductivity (log)	Value (±SE)	2.506 (0.208)	0.358 (0.154)
	P	< 0.001	0.027

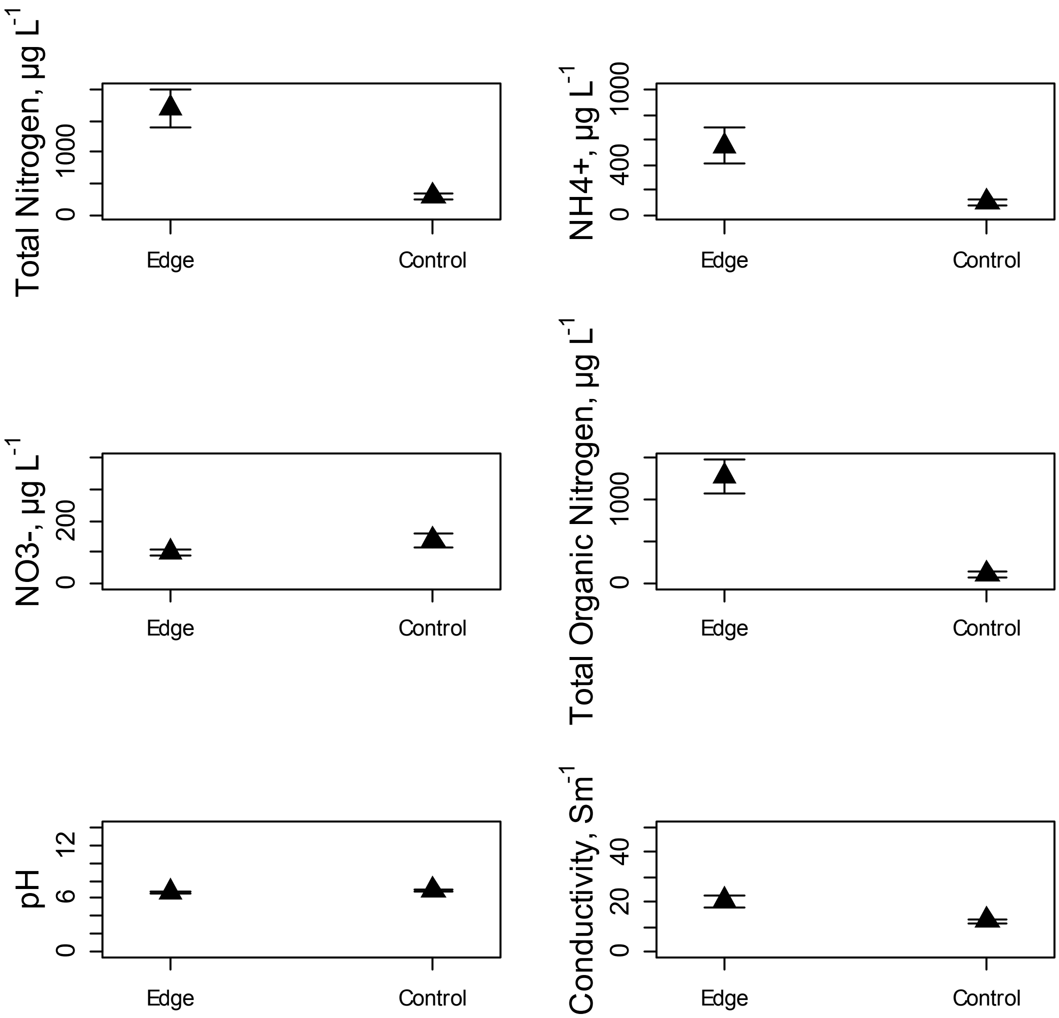

Figure 10: Mean (±1SE) concentrations of Total Nitrogen, $NH_4{}^+$, $NO_3{}^-$, Total Organic Nitrogen as well as values of pH and Conductivity in snow collected during the 1st sampling event in parks of Helsinki and Lahti. Control and next to path edge values are plotted. Note differences in units and magnitude of values on the y-axis.

3.2 Two sampling visits in Lahti

Table 2 and Fig. 11 present results of the GLMMs performed for the city of Lahti during two visits. Total Nitrogen (TN), Ammonium Ion (NH_4^+) and Total organic Nitrogen (TON) concentrations and conductivity values were significantly higher in path edge samples compared to control samples. NO_3^- and pH were higher in the control samples, but not statistically significant so. Sample values during the second visit were generally lower than the first visit. Raw parameter values are presented in Appendix 1.

Table 2: GLMM results. Coefficient (standard error, ±SE) values of each of the variables measured from snow collected in the parks of Lahti two sampling events. The Intercept includes the control samples of the first visit. Treat (Edge) represents the difference between path edge and control, and the 2nd visit column represents the difference with the 1st visit.

Parameters		Intercept	Treatment (Edge)	2nd Visit
TN (log)	Value (±SE)	5.665 (0.344)	1.707 (0.327)	-0.924 (0.283)
	P	<0.001	0.003	0.002
NH_4^+ (log)	Value (±SE)	4.627 (0.432)	1.297 (0.295)	- 0.635 (0.256)
	P	<0.001	<0.001	0.018
NO_3^-	Value (±SE)	4.932 (0.158)	-0.215 (0.142)	-0.561 (0.123)
	P	<0.001	0.14	<0.001
TON (log)	Value (±SE)	5.394 (0.629)	1.643 (0.651)	-1.181 (0.385)
	P	<0.001	0.019	0.005
pH (log)	Value (±SE)	1.964 (0.013)	-0.051 (0.015)	-0.121 (0.018)
	P	<0.001	0.092	<0.001
Conductivity (log)	Value (±SE)	2.680 (0.152)	0.355 (0.125)	-0.165 (0.109)
	P	<0.001	0.008	0.1390

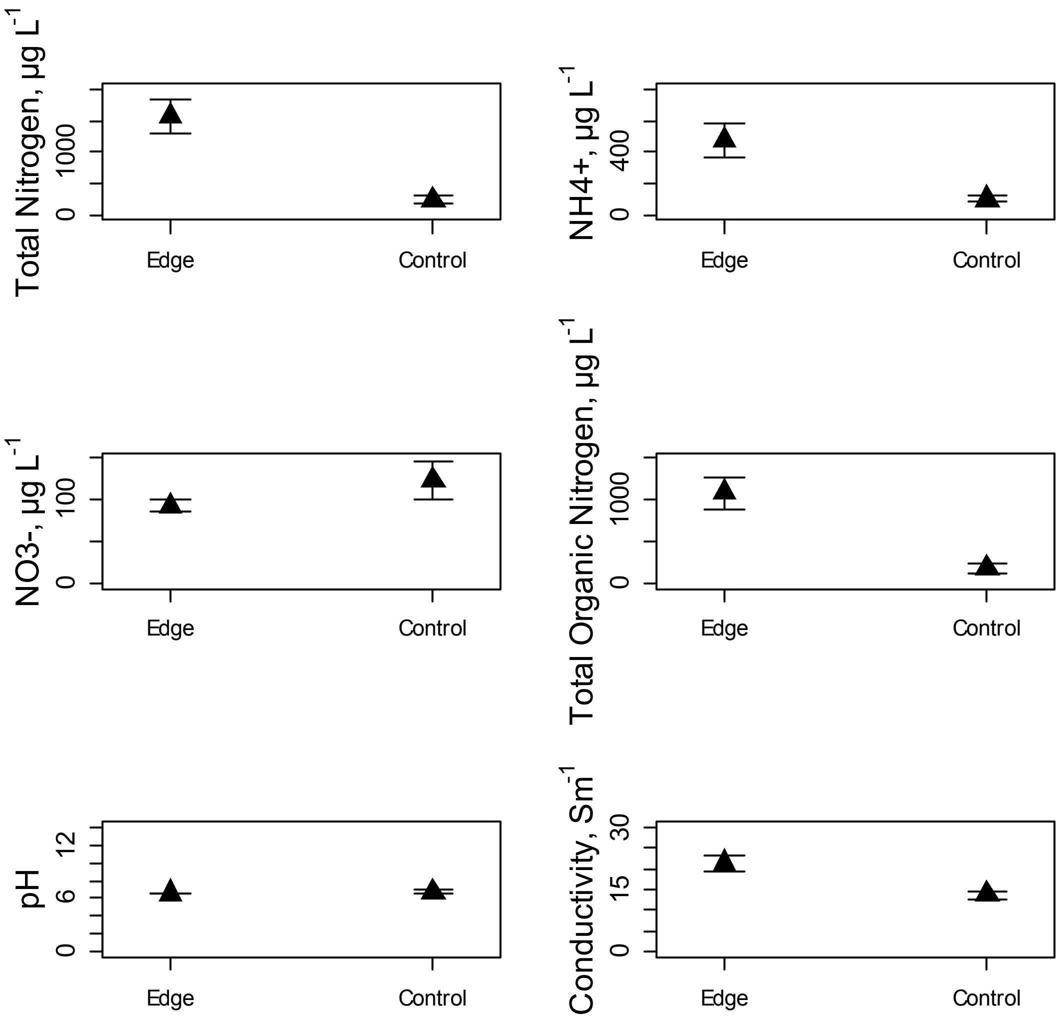

Figure 11: Mean (±1SE) concentrations of Total Nitrogen, NH_4^+, NO_3^-, Total Organic Nitrogen as well as values of pH and Conductivity in snow collected during the first and second sampling event in parks in Lahti. Control and next to path edge values are plotted. Note differences in units and magnitude of values on the y-axis.

4 Discussion

The main objective of the study was to determine if nitrogen accumulates in the snowpack of urban parks during winter and if so, does the accumulation vary spatially within the park relative to walking paths. It was my hypothesis that, activities in the park, primarily dog walking, will result in higher nitrogen levels in path-edge snow banks, relative to control sites located 8 m away from the paths. The concentration of TN, NH_4^+ and TON were significantly higher in path edge snow banks compare to the control plots, which supported my hypothesis. In contrast, the concentration of NO_3^- was lower in path-side snow banks compare to control plots, contrary to expectation and pH values were higher in control plots but not significantly different from path edge samples. Conductivity was higher in path-side samples than the control. Among the two visiting events of Lahti, samples from the first event had higher concentrations and values than the second visit for all six parameters; this is contrary to what I had expected as in the beginning I thought that these nitrogen-related compounds would accumulate in the snow as winter continues.

4.1 Concentrations of nitrogen-related compounds in urban parks

The study is presented in two ways, (i) based on a single sampling event in 10 parks in two cities and (ii) based on two sampling events in parks in Lahti only. Results showed that concentrations of TN, NH_4^+ and TON were higher in path-side snowpack and were significantly different between control and path edge snowpack for both analyses. This suggests that dog activities (urination) in urban parks can cause the accumulation of some species of nitrogen (TN, NH_4^+ ,TON) in path side snowpack and it is significantly higher than other parts of parks with no dog activities. Several previous studies on the accumulation of pollutants in snow showed that snow can trap pollutants, which lead to the accumulation of various pollutants in snow (Carrera et al., 2001; Kuoppamäki et al., 2014; Nazarenko et al., 2016; Sansalone and Glenn III, 2002). My study is in line with these findings, showing the accumulation of nitrogen species in urban park snow. Regarding the capacity of urine to increase nitrogen levels in snow, Davies et al., (2013) found the following; animal urine in snow can increase the level of nitrogen related compounds in snow, which is supporting my results for TN, NH_4^+ and TON.

The concentration of NO_3^- was lower in the path side snowpack, but the difference between path edge and control was not significant. This trend was common in both analyses. My results suggest that the concentration of NO_3^- does not vary significantly between areas with high dog activities and areas with no dog activities in urban parks. This is an exception and may need further study. My observation is that, the NO_3^- was being deposited with the snow as precipitation, and so didn't vary with in the park, while NH_4^+, TN and TON were being deposited by dogs in the path side snow. Apart from that, one reason that can be link with this is chemical transformation of nitrogen compounds in snow and sunlight. Photolysis leads nitrate and nitrite to the gas phase through several chemical transformations and finally emit to the atmosphere from snow (Jacobi and Hilker, 2007). This transformation may lead to an overall decrease in NO_3^- concentrations in snow samples. This could be another reason for NO_3^- showing a different pattern from the other nitrogen species.

Overall, my study suggests that dog activities in urban parks can accumulate nitrogen in the snowpack.

4.2 Intra-seasonal variation of nitrogen concentrations in urban snowpack

Samples from the second visit in Lahti had significantly lower concentrations of TN, NH_4^+, NO_3^- and TON compared to the first visit. Initially I expected concentrations to be higher during the second visit, due to the accumulation of dog urine during the winter season. The reason of this result could be the approximately one month gap between sampling events, during which snowmelt occurred, and thus any accumulated nitrogen being flushed from the snowpack. Several studies have shown that snowmelt during late winter and spring causes a decrease in pollutant concentrations in snowpack (Hibberd, 1984; Johannessen and Henriksen, 1978; Meyer et al., 2009; Meyer and Wania, 2008). According to Johannessen and Henriksen (1978), 50% of pollutants is released during the first 30% meltdown of snowpack. So, my results support previous studies about the release of pollutants during snowmelt, and indicates that accumulated nitrogen in urban park snowpack from dog activities are likely released to nearby water bodies including lakes and rivers (see also Hibberd, 1984; Johannessen and Henriksen, 1978; Meyer and Wania, 2008).

The release of nitrogen in water bodies can deteriorate the ecosystem and water quality. Previous studies also supporting the fact that nitrogen addition to water bodies such as lakes and rivers can cause eutrophication, alteration of the nutrient ratio and deteriorate the existing aquatic ecosystem (Anderson et al., 2002; Carpenter et al., 1998; Conley et al., 2009; Rabalais, 2002). My study suggests that dog urination in urban snow has the potential to cause problems in nearby water ecosystems.

4.3 pH and conductivity in the snowpack of urban park

My study showed that pH values were not significantly different between path edge samples and control plots. The reason that I see such pH drop in my path edge samples is because the urea in the dog urine is breaking down and producing nitric acid. I wouldn't expect to see that in the snow nearly so strongly, since the reaction would be limited due to the cold temperatures. A study based on urban park soil had found that excessive nitrogenous compounds such as ammonium and niitrate can decrease the pH in soil and my study in the snowpack of urban park is also sowing similar results (Lee et al., 2019).

In the case of electrical conductivity, my results showed significantly higher values in path edge snowpack compared to the control plots. This might mean that conductivity can be a good indicator of the presence of urine pollution in snowpack as it responded similarly to urine than most nitrogen species in this study (TN,NH_4^+ and TON). A study have shown that human urine can increase the electrical conductivity of soil (Neina and Dowuona, 2013).

I did not study the health effects of nitrogen accumulation on urban park snowpack. Previous studies have shown that contact with excessive nitrogen can be detrimental to human health (Davidson et al., 2011; Wolfe and Patz, 2002). This study can be incorporated to future studies on this health issue in urban parks due to nitrogen accumulation in snowpack as a result of dog activities.

To summarise, my study supports the general conclusion that dog urination can increase nitrogen concentrations in urban snowpack. During snowmelt, the accumulated nitrogen washes into storm water drains and, if untreated, further to nearby water bodies including lakes and ponds, potentially causing or contributing to environmental problems. The concentrations of TN, NH_4^+ and TON follow the same pattern of being higher in path edge snow, which have higher dog activities (e.g. urinating) compare to other areas of parks with little dog activities. Conductivity values reacted in a similar way. NO_3^- concentrations and pH values did not differ significantly between path edge and control plots. Further research on this topic can be done to understand the activities of dogs on urban park snowpack more clearly. Finding of this research can be helpful for park and city planners as this study results showed that dog activities in urban parks in winter can have environmental and health effects. Separate place for dog walking with a special geographical location that may constrain runoff directly to water bodies when snowmelt and awareness programs for pet owners can be arranged too. Moreover, visitors in parks during winter need to be extra cautious and should avoid to get direct contact with path edge snows as it have excess level of nitrogen according to this study.

5 Acknowledgements

This thesis was an excellent opportunity for me to enrich my research experience and I have learned a lot from the process. Firstly, I want to express my heartiest gratitude to my supervisor Dr. Johan Kotze and my co-supervisor John Allen for their utmost sincere cooperation in every stages of this thesis. It would never have be possible for me to complete the thesis without their guidance and support.

I would like to thank the efforts of Marianne Lehtonen and Dr. Jukka Pellinen who greatly helped me in performing the laboratory experiments.

I want to give special thanks to my friend Maryam Agheshlouei for reviewing my writing and giving overall guidance. Lastly, I am grateful to my parents for their unconditional support throughout my life.

References

Abdel-Shafy, H.I., Mansour, M.S., 2016. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. Egyptian journal of petroleum 25, 107–123.

Allen, J.A., 2016. Polycyclic aromatic hydrocarbon (pah) contamination in snow dump site sediments. https://doi.org/10.13140/RG.2.2.29418.00967

Anderson, D.M., Glibert, P.M., Burkholder, J.M., 2002. Harmful algal blooms and eutrophication: nutrient sources, composition, and consequences. Estuaries 25, 704–726.

Bettez, N.D., Groffman, P.M., 2013. Nitrogen deposition in and near an urban ecosystem. Environmental science & technology 47, 6047–6051.

Camargo, J.A., Alonso, Á., 2006. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment. Environment International 32, 831–849. https://doi.org/10.1016/j.envint.2006.05.002

Campbell, M.J., 1990. Membrane process and system for nitrogen production.

Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., Smith, V.H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecological applications 8, 559–568.

Carrera, G., Fernández, P., Vilanova, R.M., Grimalt, J.O., 2001. Persistent organic pollutants in snow from European high mountain areas. Atmospheric environment 35, 245–254.

Conley, D.J., Paerl, H.W., Howarth, R.W., Boesch, D.F., Seitzinger, S.P., Havens, K.E., Lancelot, C., Likens, G.E., 2009. Controlling eutrophication: nitrogen and phosphorus. Science 323, 1014–1015.

Coombes, E., Jones, A.P., Hillsdon, M., 2010. The relationship of physical activity and overweight to objectively measured green space accessibility and use. Social science & medicine 70, 816–822.

Davidson, E.A., David, M.B., Galloway, J.N., Goodale, C.L., Haeuber, R., Harrison, J.A., Howarth, R.W., Jaynes, D.B., Lowrance, R.R., Thomas, N.B., 2011. Excess nitrogen in the US environment: trends, risks, and solutions. Issues in Ecology.

Davies, T.D., Tranter, M., Jones, H.G., 2013. Seasonal Snowpacks: Processes of Compositional Change. Springer Science & Business Media.

del Saz Salazar, S., Menendez, L.G., 2007. Estimating the non-market benefits of an urban park: Does proximity matter? Land use policy 24, 296–305.

Doane, T.A., Horwáth, W.R., 2003. Spectrophotometric Determination of Nitrate with a Single Reagent. Analytical Letters 36, 2713–2722. https://doi.org/10.1081/AL-120024647

Edwards, P., Tsouros, A.D., 2006. Promoting physical activity and active living in urban environments: the role of local governments. WHO Regional Office Europe.

Fang, Y., Gundersen, P., Vogt, R.D., Koba, K., Chen, F., Chen, X.Y., Yoh, M., 2011. Atmospheric deposition and leaching of nitrogen in Chinese forest ecosystems. Journal of Forest Research 16, 341.

Finland Population (2020) - Worldometer [WWW Document], n.d. URL https://www.worldometers.info/world-population/finland-population/ (accessed 7.12.20).

Finland Population 2020 (Demographics, Maps, Graphs) [WWW Document], n.d. URL https://worldpopulationreview.com/countries/finland-population/ (accessed 7.12.20).

Galloway, J.N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.W., Seitzinger, S.P., Asner, G.P., Cleveland, C.C., Green, P.A., Holland, E.A., 2004. Nitrogen cycles: past, present, and future. Biogeochemistry 70, 153–226.

Galloway, J.N., Townsend, A.R., Erisman, J.W., Bekunda, M., Cai, Z., Freney, J.R., Martinelli, L.A., Seitzinger, S.P., Sutton, M.A., 2008. Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science 320, 889–892.

Halstead, J.A., Kliman, S., Berheide, C.W., Chaucer, A., Cock-Esteb, A., 2014. Urban stream syndrome in a small, lightly developed watershed: a statistical analysis of water chemistry parameters, land use patterns, and natural sources. Environ Monit Assess 186, 3391–3414. https://doi.org/10.1007/s10661-014-3625-9

Hartig, T., Mang, M., Evans, G.W., 1991. Restorative effects of natural environment experiences. Environment and behavior 23, 3–26.

Hibberd, S., 1984. A Model for Pollutant Concentrations During Snow-Melt. Journal of Glaciology 30, 58–65. https://doi.org/10.3189/S0022143000008492

Jacobi, H.-W., Hilker, B., 2007. A mechanism for the photochemical transformation of nitrate in snow. Journal of Photochemistry and Photobiology A: Chemistry 185, 371–382. https://doi.org/10.1016/j.jphotochem.2006.06.039

Johannessen, M., Henriksen, A., 1978. Chemistry of snow meltwater: changes in concentration during melting. Water Resources Research 14, 615–619.

Keskinen, A., n.d. Lumilogistiikan tehostaminen kaupungeissa 172.

Kuoppamäki, K., Setälä, H., Rantalainen, A.-L., Kotze, D.J., 2014. Urban snow indicates pollution originating from road traffic. Environmental Pollution 195, 56–63. https://doi.org/10.1016/j.envpol.2014.08.019

Lee, J.M., Tan, J., Gill, A.S., McGuire, K.L., 2019. Evaluating the effects of canine urine on urban soil microbial communities. Urban Ecosyst 22, 721–732. https://doi.org/10.1007/s11252-019-00842-0

Liu, X., Duan, L., Mo, J., Du, E., Shen, J., Lu, X., Zhang, Y., Zhou, X., He, C., Zhang, F., 2011. Nitrogen deposition and its ecological impact in China: an overview. Environmental pollution 159, 2251–2264.

Meyer, T., Lei, Y.D., Muradi, I., Wania, F., 2009. Organic Contaminant Release from Melting Snow. 1. Influence of Chemical Partitioning. Environ. Sci. Technol. 43, 657–662. https://doi.org/10.1021/es8020217

Meyer, T., Wania, F., 2008. Organic contaminant amplification during snowmelt. Water Research 42, 1847–1865. https://doi.org/10.1016/j.watres.2007.12.016

Miranda, K.M., Espey, M.G., Wink, D.A., 2001. A Rapid, Simple Spectrophotometric Method for Simultaneous Detection of Nitrate and Nitrite. Nitric Oxide 5, 62–71. https://doi.org/10.1006/niox.2000.0319

Na, G., Liu, C., Wang, Z., Ge, L., Ma, X., Yao, Z., 2011. Distribution and characteristic of PAHs in snow of Fildes Peninsula. Journal of Environmental Sciences 23, 1445–1451.

Särkkä, H. Näin paljon lumikaaos voi maksaa Helsingille – ”Katastrofiin ei ole varauduttu” [WWW Document], 2016. . Ilta-Sanomat. URL https://www.is.fi/kotimaa/art-2000001065258.html (accessed 7.27.20).

Nazarenko, Y., Kurien, U., Nepotchatykh, O., Rangel-Alvarado, R.B., Ariya, P.A., 2016. Role of snow and cold environment in the fate and effects of nanoparticles and select organic pollutants from gasoline engine exhaust. Environmental Science: Processes & Impacts 18, 190–199.

Neina, D., Dowuona, G.N.N., 2013. Short-term effects of human urine fertiliser and wood ash on soil pH and electrical conductivity.

Nowak, D.J., Dwyer, J.F., Childs, G., 1998. The benefits and costs of urban trees. Areas verdes urbanas en Latinoamerica y el Caribe. Centro de Agroforesterıa para el Desarrollo Sostenible, Universidad Autonoma de Chapingo, Mexico.

Pope Iii, C.A., Burnett, R.T., Thun, M.J., Calle, E.E., Krewski, D., Ito, K., Thurston, G.D., 2002. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. Jama 287, 1132–1141.

Rabalais, N.N., 2002. Nitrogen in aquatic ecosystems. AMBIO: A Journal of the Human Environment 31, 102–112.

Reese, J., 2005. Dogs and Dog Control in Developing Countries. State of the Animals 2005.

Reinosdotter, K., Viklander, M., 2005. A Comparison of Snow Quality in Two Swedish Municipalities – Luleå and Sundsvall. Water Air Soil Pollut 167, 3–16. https://doi.org/10.1007/s11270-005-8635-3

Sansalone, J.J., Glenn III, D.W., 2002. Accretion of pollutants in snow exposed to urban traffic and winter storm maintenance activities. I. Journal of Environmental Engineering 128, 151–166.

Sims, G.K., Ellsworth, T.R., Mulvaney, R.L., 1995. Microscale determination of inorganic nitrogen in water and soil extracts. Communications in Soil Science and Plant Analysis 26, 303–316. https://doi.org/10.1080/00103629509369298

Snow statistics - Finnish Meteorological Institute [WWW Document], n.d. URL https://en.ilmatieteenlaitos.fi/snow-statistics (accessed 7.14.20).

Team, R.C., 2019. R: a language and environment for statistical computing. R Foundation for Statistical Computing website.

Tilastokeskus, n.d. Population [WWW Document]. URL http://www.stat.fi/tup/suoluk/suoluk_vaesto_en.html (accessed 7.13.20).

Tzoulas, K., Korpela, K., Venn, S., Yli-Pelkonen, V., Kaźmierczak, A., Niemela, J., James, P., 2007. Promoting ecosystem and human health in urban areas using Green Infrastructure: A literature review. Landscape and urban planning 81, 167–178.

Viklander, M., 1999. Dissolved and particle-bound substances in urban snow. Water Science and Technology 39, 27–32. https://doi.org/10.1016/S0273-1223(99)00314-5

Wolfe, A.H., Patz, J.A., 2002. Reactive nitrogen and human health: acute and long-term implications. Ambio: A journal of the human environment 31, 120–125.

Appendix

Appendix 1. Data tables

a. Results of the first sampling event in Helsinki and Lahti (25-28 February,2019)

City	Treat	Park code	TN(µg/L)	NH4+ (µg/L)	NO3- (µg/L)	Total Organic Nitrogen(µg/L)	pH	Conductivity (Sm^{-1})
Helsinki	Control	35	209	64	125	20	6.48	8.9
Helsinki	Edge	35	1779	868	42	869	6.41	26.1
Helsinki	Edge	35	215	220	11	-16	6.55	14.1
Helsinki	Edge	35	4799	3190	57	1552	6.83	54.3
Helsinki	Control	41	115	54.585	44	16.415	6.49	10.7
Helsinki	Edge	41	120	89.83	52	-21.83	6.92	16.1
Helsinki	Edge	41	110	138.096	56	16.23743	6.67	20
Helsinki	Edge	41	1230.5	354.339	41	835.161	6.35	8.5
Helsinki	Control	54	320	84.465	151	84.535	6.46	16.1
Helsinki	Edge	54	205	48.238	97	59.762	6.54	12.1
Helsinki	Edge	54	105	78.755	125	11.15309	6.48	9
Helsinki	Edge	54	155.8	29.28	97	29.52	6.69	8.7
Helsinki	Control	60	282	34	56	192	6.7	9.7
Helsinki	Edge	60	1590	252	101	1237	6.39	11.5
Helsinki	Edge	60	460	144	72	244	6.44	13.1
Helsinki	Edge	60	2247	328	134	1785	6.55	16.7
Helsinki	Control	63	485	204	162	119	6.55	10.8
Helsinki	Edge	63	1345	178	155	1012	6.68	14.1
Helsinki	Edge	63	472	118	184	170	6.51	16.7
Helsinki	Edge	63	1800	424	14	1362	6.98	8
Lahti	Control	12	335	89	273	-27	7.79	11.2
Lahti	Edge	12	1449	309.73	136	1003.27	6.68	14.3
Lahti	Edge	12	1620	275.45	135	1209.55	6.94	14
Lahti	Edge	12	3076	466	167	2443	6.88	17.8
Lahti	Control	13	50	148.5	35	66.72735	6.86	13.3
Lahti	Edge	13	1057	629.137	46	381.863	6.89	42
Lahti	Edge	13	6025	1568.076	132	4324.924	6.77	60.3
Lahti	Edge	13	2320	679.2325	100	1540.768	6.78	20.3
Lahti	Control	18	285	103.342	193	-11.342	6.93	12.3
Lahti	Edge	18	447	104	99	244	6.74	37.2
Lahti	Edge	18	240	109.291	170	-39.291	6.62	12.4
Lahti	Edge	18	691	78.143	160	452.857	7.06	12.7
Lahti	Control	22	470	233.837	177	59.163	7.34	15.3
Lahti	Edge	22	5985	2659.154	78	3247.846	6.76	35.7
Lahti	Edge	22	3763	1834.35	80	1848.65	6.7	33.9
Lahti	Edge	22	1489	468	169	852	6.7	20.4
Lahti	Control	24	420	12.8	140	267.2	6.76	16.9
Lahti	Edge	24	1644	335.314	84	1224.686	6.72	10.6
Lahti	Edge	24	3143	269.0911	144	2729.909	6.72	17.3
Lahti	Edge	24	1628	219.607	95	1313.393	6.92	17.1

b. Raw data from the 2nd sampling event, only in Lahti (1-2 April,2019).

City	Treat	Park Code	TN(µg/L)	NH4+ ((µg/L))	NO3- ((µg/L))	Total Organic Nitrogen ((µg/L))	pH	Conductivity (Sm^{-1})
Lahti	Control	13	140	99.66307	85	-44.6631	6.72	11.6
Lahti	Edge	13	195	120	28	47	6.42	14.3
Lahti	Edge	13	1189	379	76	734	6.2	22.9
Lahti	Edge	13	1359.9	456.5118	47	856.3882	6.46	23.2
Lahti	Control	18	390	127.1692	56	206.8308	6.35	19.2
Lahti	Edge	18	691	114	50	527	6.5	16.8
Lahti	Edge	18	50	12.31	-3	40.69	6.28	12.3
Lahti	Edge	18	808.09	216.295	75	516.795	6.66	15.2
Lahti	Control	22	165	81	106	-22	6.2	15.2
Lahti	Edge	22	468	525	61	-118	6.44	26.2
Lahti	Edge	22	1283	92	83	1108	6.21	15
Lahti	Edge	22	2476	1125.809	49	1301.191	6.45	34.1
Lahti	Control	12	155	89	70	-4	6.27	10.7
Lahti	Edge	12	904	503	79	322	6.29	16.6
Lahti	Edge	12	440	239.176	50	150.824	6.41	19.2
Lahti	Edge	12	544.66	277.6053	64	203.0547	6.52	17.7
Lahti	Control	24	30	14	99	-83	6.05	11.2
Lahti	Edge	24	1390	120	139	1131	6.24	13.3
Lahti	Edge	24	751	156	85	510	6.21	16
Lahti	Edge	24	160	49	62	49	6.28	9.4

Park Code - Park Name

12	Ankkurinpuisto
13	Kirkkopuisto
18	Anttilanmäen puisto
22	Erkonpuisto
24	Kevätkadun puisto
35	Vanha kirkkopuisto
41	Hesperian puisto
54	Kurkipuisto
60	Munkkiniemen kartanon puisto
63	Vallilanlaakson puisto